5. Halocarbons and other Atmospheric Trace Species

B.D. HALL (EDITOR), J.H. BUTLER, A.D. CLARKE, G.S. DUTTON, J.W. ELKINS, D.F. HURST, D.B. KING, E.S. KLINE, J. LIND, L.T. LOCK, D. MONDEEL, S.A. MONTZKA, F.L. MOORE, J.D. NANCE, E.A. RAY, P.A. ROMASHKIN, AND T.M. THOMPSON

5.1. OVERVIEW

The mission of the Halocarbons and other Atmospheric Trace Species (HATS) group is to study halocarbons and other trace gases that cause chemical and radiative change in the atmosphere. The goal of HATS is to measure and interpret the distributions and trends of these species in the troposphere, stratosphere, and ocean with the best analytical instrumentation available. The species measured include nitrous oxide (N_2O); many halogenated species, such as halocarbons, fluorocarbons, perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6); organic nitrates, such as peroxyacetyl nitrate (PAN); organic sulfur gases, such as carbonyl sulfide (COS); and hydrocarbons (HCs). The halocarbons include the chlorofluorocarbons (CFCs); chlorocarbons (CCs), such as CCl_4, CH_3CCl_3, $CHCl_3$, CH_2Cl_2, and C_2Cl_4; hydrochlorofluorocarbons (HCFCs); hydrofluoro-carbons (HFCs); methyl halides (CH_3Br, CH_3Cl, and CH_3I); bromocarbons (CH_2Br_2 and $CHBr_3$); and halons.

Three primary research areas involving these trace gases are stratospheric ozone depletion, climate change, and air quality. For example, the CFCs and N_2O are major ozone-depleting and greenhouse gases. The trace gas SF_6 is a greenhouse gas with a large global warming potential, but its net warming is small because of its low concentration in the atmosphere. Short-lived halocarbons, PAN, and the HCs play an important role in global and regional pollution. PAN is a major precursor of tropospheric ozone in the remote marine atmosphere. Tropospheric COS is a relatively stable sulfur molecule that contributes to the stratospheric aerosol layer.

Research conducted by HATS in 2000 and 2001 included (1) weekly flask sampling and analysis of air from remote and continental-influenced sites, (2) operation of instrumentation for hourly, in situ measurements of trace gases at the four CMDL baseline observatories, Barrow Observatory (BRW), Mauna Loa Observatory (MLO), Samoa Observatory (SMO), and South Pole Observatory (SPO), and at four continental-influenced sites, (3) preparation and maintenance of trace gas standards, (4) participation on airborne campaigns with in situ gas chromatographs (GCs) on aircraft and balloon payloads, (5) investigation of oceanic processes that influence trace gas composition of the atmosphere, and (6) measurement of many trace gases in firn air from South Pole.

Continuing programs within HATS are based upon in situ and flask measurements of the atmosphere from the 4 CMDL baseline observatories and 10 cooperative stations (Figure 5.1). Table 5.1 lists the geographic locations and other useful information for all the sites. There are currently 14 flask sites and 8 in situ sampling sites in the HATS atmospheric sampling network.

One of the highlights of this report is that the total equivalent chlorine (Cl + Br) in the troposphere continues to decrease at about 1% yr^{-1} as a result of the Montreal Protocol [*UNEP*, 1987]. Total equivalent chlorine in the stratosphere appears to have leveled off or peaked at most altitudes. The main reason for the decline in the troposphere is that methyl chloroform (CH_3CCl_3) concentrations continued to decline to less than half of the peak levels present in 1992. However, atmospheric concentrations of the halons and CFC-12 are still increasing because of permitted production in the developing countries and the large bank of chemicals that exists in the developed countries. As a result of the halon increase, the total bromine in the troposphere and stratosphere is still increasing. Once atmospheric CH_3CCl_3 is depleted, the trend in total equivalent chlorine may significantly change, requiring further observation.

Other significant results include the global increases in atmospheric N_2O and SF_6, observed from both flask and in situ monitoring, the continued growth of the CFC replacements (HCFCs and HFCs), and the decline in the northern hemispheric concentrations of $CHCl_3$ and C_2Cl_4 as a result of the U.S. Clean Air Act. Carbonyl sulfide distributions from both in situ and flask measurements are described for the first time and show a strong seasonal cycle. A new flask station was added in 2001 at Trinidad Head, California. Airborne measurements were conducted in the upper troposphere and lower stratosphere in the northern polar region during the 1999 and 2000 Stratospheric Aerosol and Gas Experiment III (SAGE III) Ozone Loss and Validation Experiment (SOLVE) conducted from Kiruna, Sweden. The rapid-sampling airborne gas chromatograph was also used to measured CFCs, halons, and chlorinated solvents in Russia along the trans-Siberian railway during June-July 2001 in a collaboration with Russian and German scientists. The construction of the next-generation airborne GC with electron capture and mass spectrometric detection was funded by the National Aeronautics and Space Administration (NASA) Instrument Incubation Program to measure trace gases, including hydrocarbons and organic nitrates, that influence atmospheric chemistry in the upper troposphere. An in situ GC system, equipped with one mass selective detector and two electron capture detectors, is being built for the new U.S. West Coast sampling site (Trinidad Head, California, or elsewhere on the U.S. West Coast) to monitor pollution originating in Asia and transported over the Pacific Ocean.

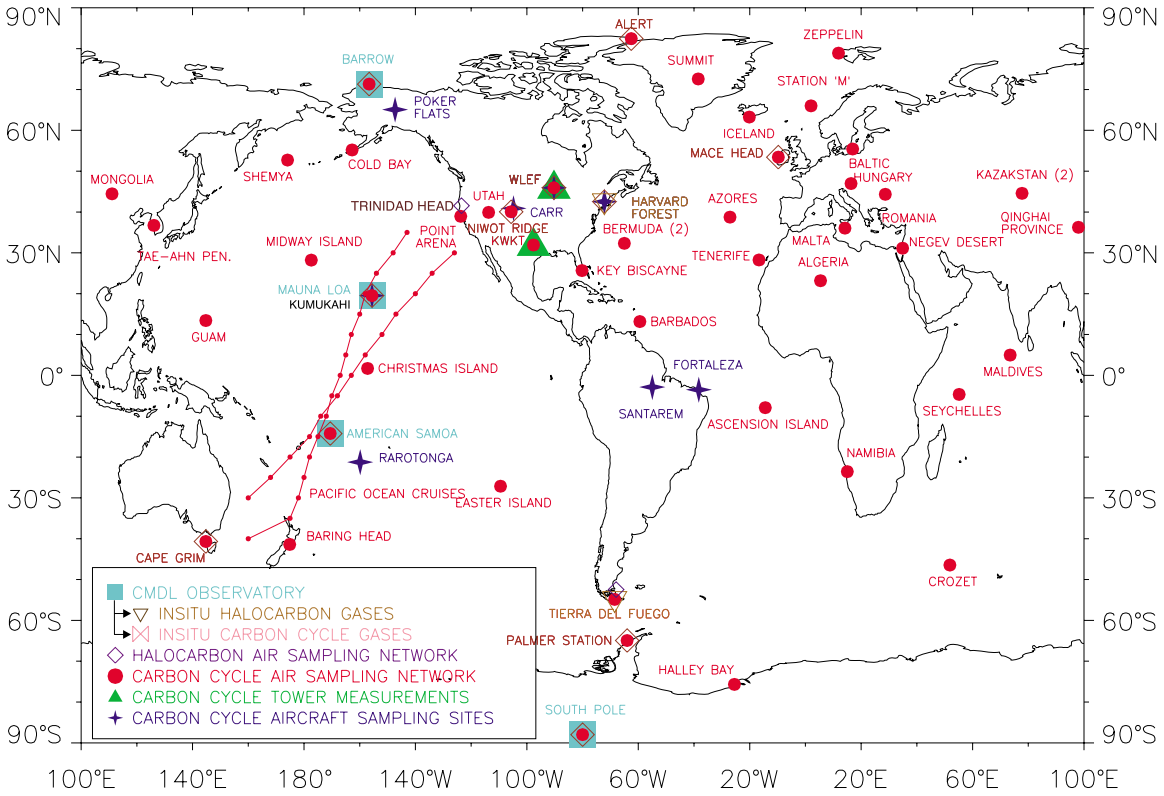

Fig. 5.1. Geographic locations of stations in the CMDL/HATS flask and in situ networks, along with CMDL/Carbon Cycle Greenhouse Gases (CCGG) stations (N_2O and SF_6 collected in glass flasks) and tower sites (triangles, future in situ halocarbon measurement).

TABLE 5.1. Geographic and Network Information for HATS Network Sites

Code	Station	Latitude	Longitude	Elevation (m)	LST – GMT (h)	Type
ALT	Alert, Northwest Territories, Canada*	82.45°N	62.52°W	210	-4	F
BRW	Point Barrow, Alaska	71.32°N	136.60°W	11	-9	F, I
MHD	Mace Head, Ireland (University College)	53.33°N	9.90°W	42	0	F
LEF	WLEF tower, Wisconsin (CMDL/CCGG)	45.95°N	90.28°W	470	-6	F, I
HFM	Harvard Forest, Massachusetts (Harvard University)	42.54°N	72.18°W	340	-5	F, I
THD	Trinidad Head, California (Humbolt State University)	41.05°N	124.15°W	109	-8	F
NWR	Niwot Ridge, Colorado (University of Colorado)	40.04°N	105.54°W	3013	-7	F, I
ITN	WITN tower, North Carolina (CMDL/CCGG)†	35.37°N	77.39°W	9	-5	F, I
MLO	Mauna Loa, Hawaii	19.54°N	155.58°W	3397	-10	F, I
KUM	Cape Kumukahi, Hawaii	19.52°N	154.82°W	3	-10	F
SMO	Tuluila, American Samoa	14.23°S	170.56°W	77	-11	F, I
CGO	Cape Grim, Tasmania, Australia‡	40.41°S	144.64°E	94	+10	F
TDF	Ushuaia, Argentina (WMO GAW station)§	54.82°S	68.32°W	10	-3	F, I
PSA	Palmer Station, Antarctica¶	64.92°S	64.00°W	10	+12	F
SPO	South Pole, Antarctica	89.98°S	102.00°E	2841	+12	F, I

F, flasks; I, in situ.
*Cooperative site with Environment Canada.
†Site's flask and in situ GC instrument closed down on June 12, 1999.
‡Cooperative site with Commonwealth Scientific and Industrial Research Organization (CSIRO) and Bureau of Meteorology, Australia.
§Began collecting data in November 2001.
¶Only glass flasks used.